twofold axis makes a bridge over two molecules through the hydrogen bonds to the carboxyl group [$O(H_2O)\cdots O(1)$ 2·83 Å].

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3,4-Dimethyl-5-thioformylimino-4*H*-1,2,4-thiadiazoline

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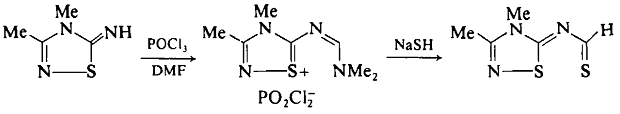
Abstract. $C_5H_7N_3S_2$, monoclinic, $P2_1/m$, $a = 7{\cdot}367$ (2), $b = 6{\cdot}157$ (2), $c = 8{\cdot}629$ (3) Å, $\beta = 93{\cdot}20$ (3)°, $U = 390{\cdot}79$ Å^3, $M_r = 173{\cdot}26$, $D_c = 1{\cdot}472$ Mg m^{-3} for $Z = 2$, $F(000) = 180$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, μ(Mo $K\alpha$) = 0·544 mm^{-1}, $R = 0{\cdot}0945$ for 641 reflections. The molecules of the title compound are disordered across the mirror plane with site-occupation factors of 0·5. The title compound does not contain a hypervalent S atom.

Introduction. Treatment of the imine (I) with phosphoryl chloride in dimethylformamide solution yielded the Vilsmeier salt (II), which reacted with sodium hydrogen sulphide solution to give the title compound (III) (Mitchell, 1979):



(I) (II) (III)

Crystals suitable for X-ray investigation were provided by Professor D. H. Reid and Dr J. A. Mitchell.

Data were collected using a Stoe STADI-2 two-circle automatic diffractometer with graphite-crystal-monochromatized Mo $K\alpha$ radiation for a crystal of dimensions $0{\cdot}2 \times 0{\cdot}4 \times 0{\cdot}2$ mm mounted about **b**. The intensities of 840 reflections in the quadrant $\pm h,+k,+l$ with $2° \leq \theta \leq 30°$, k 0–9 ($0 \leq \mu \leq 31{\cdot}294°$) were measured using the ω–2θ scan mode with a step width of 0·01° in ω, a time of 1·0 s per step and 120–140 steps per scan. Backgrounds were measured at both ends of the scan for a time of (scan time/2). Standard reflections were measured every 30 reflections and showed only small random deviations from their means. Lorentz and polarization corrections were applied to the data, but no corrections for absorption were made. Systematic absences: $0k0$, $k \neq 2n$ indicated the space group to be $P2_1$ (C_2^2, No. 4) or $P2_1/m$ (C_{2h}^2, No. 11).

The E statistics strongly suggested centrosymmetry, although $P2_1$ was thought the more likely space group since $Z = 2$. The structure was solved in $P2_1$ using *SHELX* 76 (Sheldrick, 1976). The best E map gave the positions of all the non-H atoms for two molecules related by an apparent mirror plane, indicating a disordered structure: other solutions were similar. An identical structure solution was obtained by use of *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Initial refinement was carried out, using *SHELX* 76, in $P2_1$, with the least-squares matrix blocked so that the two independent molecules refined separately in alternate cycles. A common site-occupation factor (s.o.f.) was refined for each molecule, but the sum of the two s.o.f.'s was constrained to be unity. The two s.o.f.'s refined to values, identical within experimental error, of 0·5 [0·488 (14) and 0·512 (14)]. Refinement was therefore continued in $P2_1/m$, with the s.o.f.'s of all atoms fixed at 0·5. Three cycles of full-matrix least-squares refinement with individual isotropic temperature parameters for all non-H atoms yielded an $R(=\sum\Delta/\sum F_o,\ \Delta = |F_o - |F_c||)$ of 0·1619 and an $R_G[=(\sum w\Delta^2/\sum wF_o^2)^{1/2}]$ of 0·1722 for 641 reflections with $F_o \geq 4\sigma(F_o)$. The introduction of anisotropic temperature parameters for the two S atoms in three further cycles of refinement reduced R to 0·1159 and R_G to 0·1241. Weighting

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schemes $w = [\sigma(F_o)^2 + gF_o^2]^{-1}$ were tried for various fixed values of g, but none gave as satisfactory results as unit weights. Therefore no weighting scheme was used. The introduction of anisotropic temperature factors for all other non-H atoms except N(3) and C(5) (which lay close to the mirror plane) in three further cycles of refinement reduced R to 0·0945 and R_G to 0·0956. No H atom positions could be located from a final difference map and thus no H atom positions were included in the calculations.

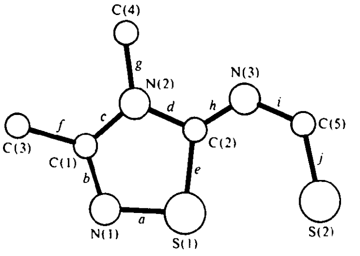

Fig. 1. The molecule showing the numbering of the atoms and bonds.

Table 1. *Fractional atomic coordinates* (×10⁴) *and equivalent isotropic temperature parameters* (Å², × 10³)

The equivalent isotropic parameters are defined as the geometric mean of the diagonal components of the diagonalized matrix of U_{ij}.

	x	y	z	U
S(1)	1837 (4)	6442 (5)	3786 (3)	45 (1)
S(2)	2982 (5)	4884 (7)	931 (3)	64 (2)
N(1)	1185 (10)	6986 (17)	5562 (10)	49 (7)
N(2)	2644 (11)	3745 (14)	5868 (9)	34 (4)
N(3)	3631 (8)	2743 (23)	3507 (7)	37 (2)*
C(1)	1724 (13)	5405 (19)	6555 (12)	38 (6)
C(2)	2835 (11)	3976 (16)	4324 (10)	32 (5)
C(3)	1336 (16)	5363 (23)	8204 (11)	52 (7)
C(4)	3302 (15)	1810 (16)	6695 (13)	44 (6)
C(5)	3758 (12)	2891 (20)	2001 (10)	45 (3)*

* N(3) and C(5) were only refined isotropically (see text).

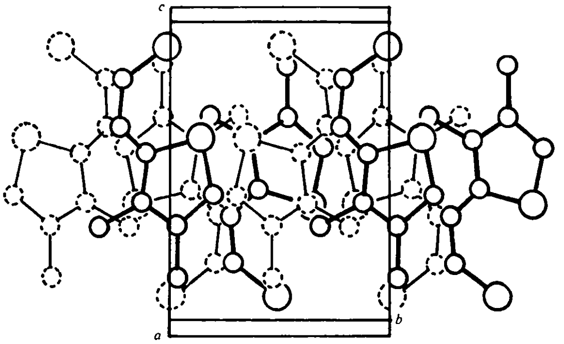

Fig. 2. The contents of the unit cell: pairs of molecules, each of s.o.f. 0·5, which are related by the mirror plane are shown in full and broken lines respectively. The figure includes all molecules whose centres lie between 0 and 1 in x, and between −0·5 and +1·5 in y and z.

Table 2. *Bond lengths* (Å)

a	1·665 (9)	*e*	1·739 (10)	*h*	1·209 (13)
b	1·342 (14)	*f*	1·467 (13)	*i*	1·311 (10)
c	1·379 (13)	*g*	1·457 (12)	*j*	1·620 (12)
d	1·355 (11)				

Table 3. *Bond angles* (°)

ab	110·6 (7)	*cf*	122·1 (11)	*dh*	126·0 (10)
ae	94·0 (5)	*cg*	123·6 (8)	*eh*	127·2 (8)
bc	113·5 (8)	*de*	106·7 (7)	*hi*	126·7 (12)
bf	124·4 (10)	*dg*	121·1 (9)	*ij*	125·1 (9)
cd	115·2 (9)				

Table 4. *Least-squares plane and distances* (Å, ×10³) *of atoms from the plane*

The plane is defined in orthogonal ångström coordinates by the equation: $Ax + By + Cz + D = 0$.

Plane: S(1), N(1), N(2), C(1), C(2)

A: −0·856 (8), B: −0·475 (6), C: −0·202 (4), D: 0·353 (12)

Distances: S(1), −9 (12); N(1), 8 (14); N(2) −7 (15); C(1), −2 (16); C(2), 10 (15); C(3), 36 (17); C(4), 34 (16); N(3) −24 (14); C(5), 52 (15); S(2) 102 (13)

In the final cycles of refinement 81 parameters were simultaneously varied, comprising 30 positional coordinates, 48 anisotropic temperature factor components, two isotropic temperature factors, and one overall scale factor: a final difference map showed no significant residual electron density. Complex neutral-atom scattering factors were used for all atoms (Cromer & Mann, 1968; Cromer & Liberman, 1970). The reductions in R_G at all stages of the refinement were significant at the 99·5% level (Hamilton, 1965).

The final atomic coordinates are given in Table 1.* These, together with the full covariance matrix, were used to calculate the bond lengths and bond angles given in Tables 2 and 3. The least-squares plane calculated for the heterocycle is given in Table 4. Fig. 1 shows the molecule and the numbering scheme for atoms and bonds. Fig. 2 shows the unit-cell contents.

Discussion. The distances S(1)–N(1) 1·665 (9) and S(1)···S(2) 2·817 (5) Å show the structure to be (III) rather than containing a hypervalent S atom as (IV).

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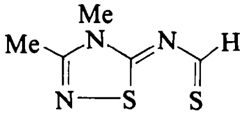
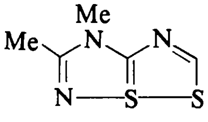
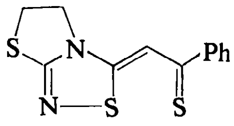
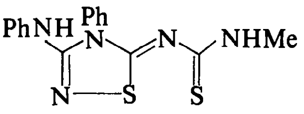
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35986 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

This confirms the structure (as III) proposed on the basis of ^{1}H NMR data (Mitchell, 1979).


(III)

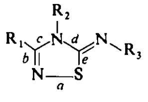

(IV)


(V)


(VI)

The S—N and S···S distances are similar to those in (V) [S—N 1·727, S···S 2·750 Å (Glidewell, Holden & Liles, 1980)] and (VI) [S—N 1·697 (10) and S···S 2·822 (5) Å (Cuthbertson & Glidewell, 1981)], but the S—N distance is shorter, and the S—S distance longer than in compounds containing a hypervalent S atom in the centre of an NSS chain; S—N range 1·779–1·863, S—S range 2·435–2·497 Å (see Glidewell *et al.*, 1980). The geometry of the 1,2,4-thiadiazoline ring is similar to those reported for (V), (VI), (VII) (Butler, Glidewell & Liles, 1978), (VIII) (L'Abbé, Verhelst, Toppet, King & Briers, 1976) and (IX) (Sato, Kinoshita, Hata & Tamura, 1972) (Table 5).

Table 5. *The geometries of* 1,2,4-*thiadiazoline rings* (Å)



	R$_1$	*R*$_2$	*R*$_3$
VII	PhNH	Ph	H
VIII	Ph	PhCH$_2$	$SO_2C_6H_4CH_3$
IX	MeNH	Me	COMe

	a	*b*	*c*	*d*	*e*
III	1·67 (1)	1·34 (1)	1·38 (1)	1·36 (1)	1·74 (1)
V	1·73 (1)	1·30 (1)	1·39 (1)	1·37 (1)	1·72 (1)
VI	1·697 (10)	1·303 (17)	1·403 (16)	1·407 (14)	1·754 (13)
VII	1·691 (3)	1·294 (4)	1·386 (4)	1·402 (4)	1·761 (4)
VIII	1·68	1·30	1·39	1·36	1·73
IX	1·685	1·29	1·39	1·36	1·725

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Structure of 3-Methyl-6-(5-phenyl-1,2-dithiol-3-ylideneamino)pyridine

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Abstract. $C_{15}H_{12}N_2S_2$, orthorhombic, *Pbca*, a = 11·918 (1), b = 30·751 (5), c = 7·196 (1) Å, U = 2634·8 Å^3, M_r = 284·40, D_c = 1·432 Mg m^{-3} for Z = 8, $F(000)$ = 1184, Mo *Kα* radiation, λ = 0·71069 Å, μ(Mo *Kα*) = 0·337 mm^{-1}; R = 0·0700 for 682 reflections. The title compound does not contain a hypervalent S atom.

Introduction. The title compound (III) was obtained from the reaction of 3-chloro-5-phenyl-1,2-dithiol-1-ium chloride (I) with 2-amino-5-methylpyridine (II) (Mitchell, 1979). Crystals suitable for X-ray in-

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